GRAFT POLYMERIZATION. IX. IMPROVED DISTRIBUTION OF GRAFTED POLYMERS IN SIDE LEATHER*

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Abstract

Although sheepskins and cattlehides have the same chemical composition, they differ in physical characteristics. Sheepskins are thinner than cattlehides and their structure is more open. Thus, graft polymerization techniques that were highly effective on sheepskins gave poor stratigraphic polymer distribution in cattlehides. Poor polymer distribution appeared as a sandwich effect with polymer restricted to shallow layers near each surface. Good polymer distribution more nearly resembled a fatliquored skin in that polymer was present throughout the skin, but in lesser amounts in the midcorium than at the grain and flesh surfaces. Study of the factors affecting the rate and completeness of persulfate ion penetration into sides in the blue led to means of greatly improving the polymer distribution. The depth of penetration by persulfate ion, visually determined when starch/iodide solution was applied to cut edges of the treated chrome stock, depended upon the concentration of the persulfate ion and length of treatment. This absorbed ion was not readily extractable with water and could be used in a separate step as part of a redox couple to initiate the graft polymerization. The stratigraphic distribution of the polymer in the products was determined in stained sections examined by light microscopy. Chemical analyses were used to determine the total and bound polymer content of the grafted leathers.

Introduction

The radical-initiated grafting of vinyl monomers onto chrome-tanned and untanned collagen has been investigated by a number of researchers. An extensive study (1) was made to optimize the conditions for such grafting of chrome-

* Presented at the 75th Annual Meeting of the American Leather Chemists Association, Oconomowoc, Wisconsin, June 17-21, 1979.

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tanned sheepskin. The goal was a complete conversion of monomer to polymer with a high graft efficiency. In addition, a uniform polymer distribution was sought. Essentially these goals were achieved. Although the procedure was successful on sheepskin, its application to side leather gave poor stratigraphic polymer distribution.

We reasoned that the absence of polymer in the midcorium of side leather might reflect a lack of initiation in this region rather than a lack of reaction or of monomer accessibility. This explanation would be consistent with the less open structure of side leather. If the initiating radical did not penetrate to the midcorium during the time period of the grafting reaction, graft polymer would not form there.

It is not practical to determine the rate or depth of penetration of the free radical into the hide. However, its precursor, the persulfate ion, can be visually located with a starch-potassium iodide indicator solution. We had previously reported (1) on the ability of blue stock to absorb persulfate ion in such a manner that it was not desorbed by water but was still able to take part in an *in situ* redox couple. In the present work we made use of those techniques to verify our speculations and to obtain a much improved polymer distribution in 5-oz side leather. We also examined the effect of time on the ability of absorbed persulfate ion to initiate graft polymerization in blue stock.

Materials

Commercially chrome-tanned 5-oz cattle sides were obtained from various tanneries. Methyl methacrylate,* inhibited with 10 ppm of the monomethyl ether of hydroquinone, was used as received.

Histological Methods

Frozen sections of the grafted cowhide were cut on the sliding microtome at 50 to 100 microns. Sections were extracted with hot methanol for 1 hr to remove most of the natural fat and any fatliquor present. In addition, sections were extracted with cold benzene for 1 hr to remove residual homopolymer, even though the original pieces were thoroughly extracted before being sectioned.

Oil Red O was dissolved in isopropyl alcohol, 0.5 to 1 g/100 ml, and 12 ml of the solution was diluted with 8 ml of water. This emulsion was allowed to stand for 10 min, then filtered before use. Sections of hide were dipped into 60 percent isopropyl alcohol and then put into the filtered emulsion. After 10 min the red color characteristic of fat was produced. The time was extended to 4 hr with butyl acrylate and to 6 hr with methyl methacrylate for full development of the color, although good color was produced in shorter periods.

Chemical Analysis

Gas chromatography was used to determine the amount of unreacted methyl methacrylate in the float at the end of each experiment. Total and bound

* Appropriate care must be taken in handling all monomers because of the possible flammability and toxic nature of these chemicals.

polymer values of the leathers were determined as previously reported (2). A modified iodometric titration (1) was used to determine the amount of potassium persulfate in the various floats.

Results and Discussion

Absorption and Distribution of Persulfate

The first phase of the investigation was to determine the rate and extent of penetration by $K_2S_2O_8$ into 5-oz blue stock. Since the water content of blue stock can vary, depending on its source and length of storage, the quantities of chemicals used were based on the average dry weight for a given lot of blue stock.

Persulfate levels of 1, 2, 3, 4, and 5 percent were used in 800 percent floats. The blue stock and floats were tumbled end-over-end at room temperature. At various times, the jar was opened and, after the blue stock was lightly blotted, a section was taken and the starch/iodide indicator was applied to visualize the depth of penetration of the persulfate ion. An aliquot of the remaining float was analyzed for its remaining persulfate content. After allowing for the water introduced into the system by the blue stock, a simple calculation gave the percent persulfate absorption. The results are shown in Figure 1. Because of the size of the aliquot used for analysis and the use of the starch/KI indicator on the blue

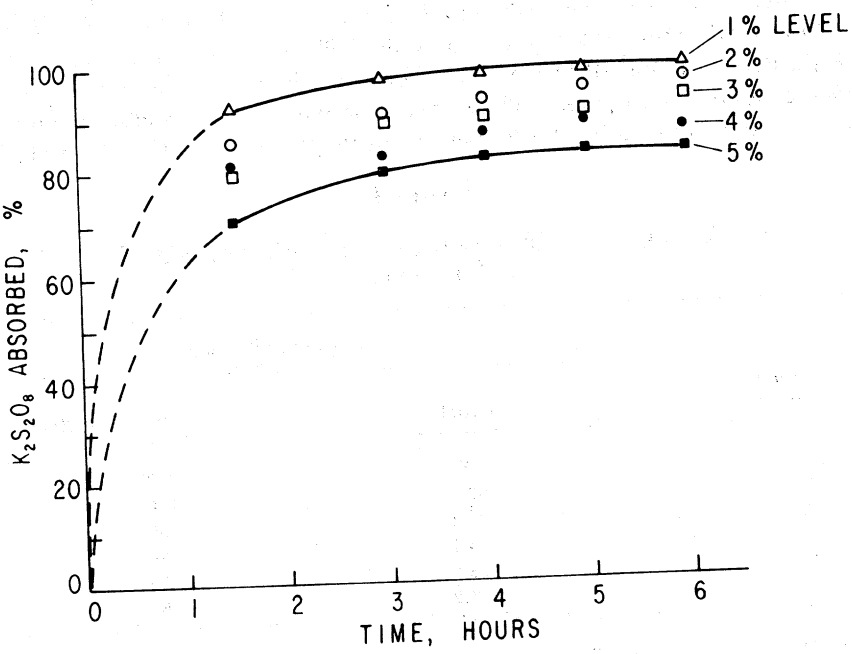

FIGURE 1.—Absorption of $K_2S_2O_8$ by blue stock.

stock, each data point was obtained by a separate experiment. The longest time interval used was 6 hr, since persulfate absorbence had leveled off by then.

Figure 1 shows that absorption of the persulfate at the 1- and 2-percent levels was at least 95 percent in 4 hr and 97 to 100 percent in 6 hr. But these levels were too low for the blue stock ever to be fully penetrated by the persulfate. Less of the persulfate added was absorbed as the level increased, until at 5 percent the absorption was only about 85 percent after 6 hr. Penetration, on the other hand, was complete after 4 to 5 hr at the 3-percent level, and after 1.5 to 3 hr at the 4- and 5-percent levels.

Absorption of persulfate by sheepskins was much faster; 95 percent of the persulfate at the 4-percent level was absorbed by sheepskins in 2 hr, whereas in this time side leather absorbed only about 75 percent.

To demonstrate that side leather would absorb persulfate ion in such a manner that simple water extraction would not remove significant amounts, new samples were prepared. The same levels and floats were used again to treat 5-oz blue stock for 6 hr. Each piece was blotted and then tumbled in a fresh float of the same size for 2 hr. Iodometric analysis of the floats was used to measure the persulfate ion absorbed by the side leather and also the amount reextracted by water in a second float. These results are shown in Table I in terms of the efficiency of the absorption before and after extraction for 2 hr. The ability of the blue stock to absorb and hold the persulfate ion can be more fully appreciated if one converts these efficiency values to the actual weight percent values. Thus, by multiplying the efficiency of uptake and the level offered, one obtains the actual weight percent absorbed by the stock. For example, at the 5-percent level, the stock contained 4.16 percent of its weight as potassium persulfate before extraction and still contained 4.02 percent of its weight after a 2-hr extraction.

TABLE I

RESISTANCE TO WATER EXTRACTION OF $K_2S_2O_8$ ABSORBED ONTO 5-OZ BLUE STOCK

$K_2S_2O_8$ offered[a]	Efficiency of Absorption	
	Initial	After Extraction[b]
%	%	%
1	100	100
2	97.1	96.9
3	93.7	92.8
4	88.6	86.5
5	83.2	80.3

[a] Based on average dry substance.
[b] After 2 hr tumbling in 200% float.

With the more usually applied 4-percent level, the values were 3.54 percent and 3.46 percent, respectively. Thus, the absorbed persulfate ion took part in the redox couple within the leather, rather than being extracted by the float to react there. This finding parallels and confirms data obtained in the earlier (1) sheepskin study. However, because of the difference in structure as well as the thickness of the two substrates, side leather took longer to absorb a given amount of persulfate. This gave strong support to the proposed reason for the poor stratigraphic polymer distribution seen in side leather when the sheepskin recipe was used for grafting.

Also in the earlier study with sheepskin, no loss of shrink temperature was observed, thus indicating that the chrome tannage was not adversely affected. At that time the absorbed persulfate could initiate polymerization when the necessary reductant and inert atmosphere were provided. It was not known how long this persulfate would be effective.

GRAFTING

For the grafting studies, the 5-oz blue stock was pretreated as described above for 6 hr with persulfate levels of 1, 2, 3, 4, and 5 percent. The stock was then treated with Emulphogene 840 BC instead of with Triton X100. Piirma *et al.* (3) have shown that Triton X100 has a benzylic hydrogen capable of forming peroxides which could lower the polymer molecular weight. Then the reductant sodium bisulfite* was applied in three different molar ratios. Since earlier studies on sheepskins (1) had shown that less than a stoichiometric amount of the reductant gave best results in terms of total and bound polymer, molar ratios of 0.18, 0.50 (theory), and 1.00 were selected in extending this work to 5-oz blue stock. The amount of sodium bisulfite needed to give these molar ratios was determined on the basis of the persulfate absorbed (since not all the persulfate offered was absorbed, except at the 1-percent level). Then the monomer methyl methacrylate was applied. Purging with dry ice and tumbling followed applications of both the reductant and the monomer.

The recipe used for these graft polymerizations was as follows (percentages based on average dry substance):

	Percent
6-hr pretreatment, 5 levels of $K_2S_2O_8$	100
Float	800
Emulphogene 840 BC	0.5
$NaHSO_3$ (molar ratios 0.18, 0.50, 1.00)	
Purge with dry ice**	
Tumble 30 min	33.3
Methyl methacrylate	
Purge with dry ice	
Tumble 30 min	

* To minimize release of SO_2, contact of sodium bisulfite with acids must be avoided.

** Caution: All dry ice should have disappeared from the float before the jar is sealed.

TABLE II

EFFECT OF VARIOUS MOLE RATIOS OF $NaHSO_3$ ON GRAFTING WITH ABSORBED $K_2S_2O_8$

$K_2S_2O_8$ Level	$NaHSO_3$	Graft Efficiency	Monomer Conversion
%	molar ratio	%	%
1	0.18	64	90
	0.50	64	96
	1.00	52	99
2	0.18	71	99 +
	0.50	48	99 +
	1.00	35	99 +
3	0.18	74	99 +
	0.50	40	99 +
	1.00	36	99 +
4	0.18	60	99 +
	0.50	40	99 +
	1.00	30	99 +
5	0.18	54	99 +
	0.50	34	99 +
	1.00	29	99 +

The graft efficiencies and percentages of monomer conversion obtained with the three molar ratios of sodium bisulfite for each of the five levels of persulfate pretreatment are shown in Table II.

Except for the first two runs at the 1-percent level of potassium persulfate, all floats showed only traces of methyl methacrylate monomer after tumbling 24 hr. This length of time was a matter of experimental convenience, since experience has shown that the reaction is as complete in 2 to 6 hr. The actual time for completeness of reaction depends more on the monomer(s) used than on the amount. Methyl methacrylate is one of the more reactive monomers used, but the incomplete monomer-to-polymer conversion at these two lowest levels of initiation must be considered unsatisfactory, even though the graft efficiencies were good.

In general, the data in Table II point up two trends. First, increasing the persulfate level has less effect on monomer-to-polymer conversion and graft efficiency than the molar ratio of reductant to oxidant. Incomplete conversion occurs only at the lowest persulfate level and the lowest molar ratio of reductant to oxidant. In fact, the very small amounts of the reductant, sodium bisulfite, and its low concentration in the float may be the cause of this incomplete reaction.

Collagen is a spatially fixed, mixed-bed deionizing resin in the sense that it has amino and carboxyl side chains. Some bisulfite ion may be bound and may not be able to diffuse further to react with the persulfate ions already in the leather. In fact, this type of absorption is the probable means of holding the absorbed persulfate ion that has been shown to be resistant to aqueous extraction. The second trend is that regardless of the persulfate level, the highest graft efficiency was obtained with the 0.18 molar ratio value, with the graft efficiency peaking at about the 3-percent persulfate level. This also was the best for sheepskin in terms of monomer conversion and graft efficiency (1). The effect is more related to the chemistry involved than to the differences between skin and hide structure. At least one other investigator studying latex formation (4) has noticed that less than stoichiometric amounts of reductant gave improved yields.

Effect of Storage on Pretreated Stock

The next phase of the study was to determine whether graft polymerization could be successfully performed on pretreated blue stock that had been kept in storage. After pretreatment, samples were stored in a refrigerator rather than preserved with a fungicide, which might bias the results. Although this type of blue stock is not currently an item of commerce, the industrial use of graft polymerization might make it so, and it would be useful to have information on its storage life.

In view of the consistent superiority of the 0.18 molar ratio of sodium bisulfite to persulfate, both on sheepskins and freshly pretreated side leather, this ratio was used in treating the stored samples at every level of persulfate except 1 percent, where a molar ratio of 0.50 was used. Polymer formation in the samples, when treated by graft polymerization both immediately after pretreatment and after storage for 3 and 6 months, is shown in Table III. This table shows that as the storage time increased, the preabsorbed persulfate ion lost its ability to take part in a redox-initiated polymerization.

Three months storage caused failure at the lowest three persulfate levels, and even the two highest levels were ineffective after six months of storage. These two highest levels were still ineffective when offered additional reductant. Sections from these samples were tested for persulfate with starch/iodide indicator. The results were negative. While the failure of the persulfate to inititate polymerization was obvious, the explanation is now only conjecture. The stored blue stock still withstood a 1-min boil, as did the control. The pH of the blue stock was essentially the same for stored, treated, or control leather; the values ranged from 3.4 to 3.6. Whether coincidental or not, the successful grafting obtained after three months storage of side leather gave the same total and bound polymer as obtained when grafted immediately. It is possible that the persulfate ion may be absorbed gradually into the chrome complex. The unchanged boil test for control and treated leather shows that the chrome complex is still an effective tanning agent. The lack of ability to form a viable redox couple shows

that the persulfate ion is either unavailable to the reductant in the physical sense, or that it has been chemically changed.

TABLE III

USE OF PREABSORBED $K_2S_2O_8$ IN A REDOX COUPLE AND EFFECT OF STORAGE TIME ON TOTAL POLYMER

$K_2S_2O_8$ Level*	$NaHSO_3$: $K_2S_2O_8$	Total Polymer (Theo. 24-28%) Formed After:		
		Immediate Use	3 Months Storage	6 Months Storage
%	molar ratio	%	%	%
1	0.5	17.1	0	—
2	0.18	24.1	0	—
3	0.18	24.5	0	—
4	0.18	26.2	26.4	0
5	0.18	27.7	24.8	0

* Based on average dry substance and pretreated for 6 hr.

HISTOLOGY

Until recently, chemical analysis has been depended upon to determine the polymer present in grafted leathers. While this satisfactorily reveals the bulk polymer, it gives no indication of its stratigraphic distribution throughout the sample. We have used Oil Red O staining as a means of detecting polymer stratigraphically in cross sections of leather samples impregnated with grafted polymer. Fat stains are not specific for polymers, but they are taken up by polymers. The validity of such a technique has been shown by correlations with stratigraphic Kjeldahl nitrogen analyses of leather before and after grafting. The colored areas seen in fat-stained sections under the light microscope correspond to zones containing polymer as determined by the nitrogen analyses. Prior to the staining, the samples must be extracted with methyl alcohol to remove natural fat, which can interfere with the determination. This solvent does not affect the polymer.

Although not quantitative, the staining method shows the general presence or absence of polymer. The Oil Red O stain disclosed polymer zones that corresponded to the depth of penetration by the persulfate ion in the pretreatment. At the lower levels of persulfate offerings, where the starch/iodide test showed incomplete penetration of the persulfate (in spite of 97 to 100 percent absorption), the fat staining of the leather sections after grafting showed correspondingly less polymer. Similarly, at the higher persulfate ion levels, good

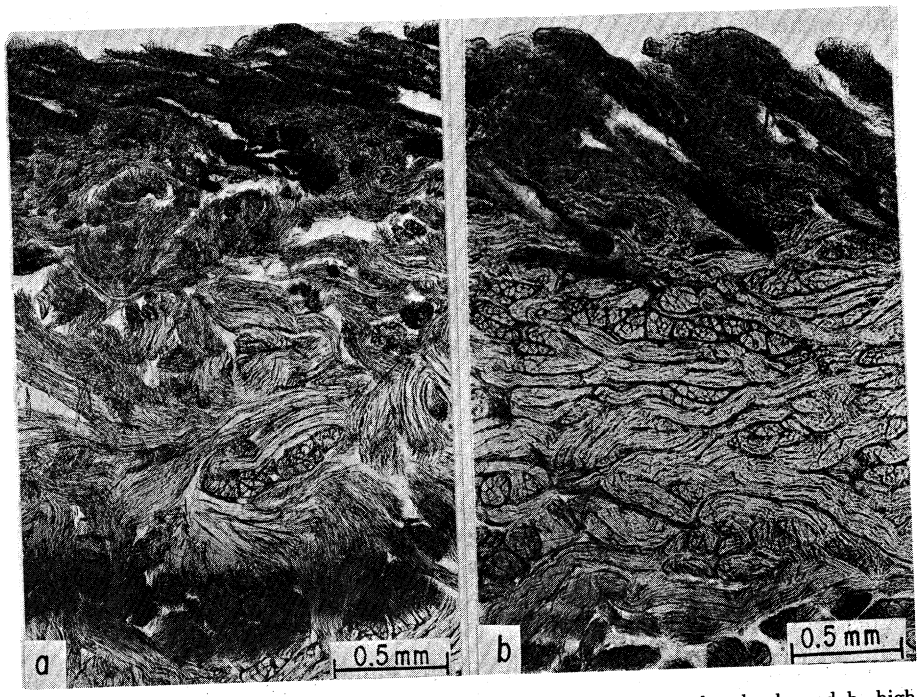

FIGURE 2.—Polymer distribution resulting from use of $K_2S_2O_8$ at: a, low level; and b, high level.

persulfate penetration and good polymer formation were indicated by both the starch/iodide and fat staining techniques. Even in black and white, the photomicrographs shown in Figure 2 make the differences in polymer formation evident between samples with low (a) and high (b) levels of persulfate.

Although from chemical analysis alone it appears that the 3-percent persulfate level is adequate, the staining experiments showed that somewhat better polymer distribution was achieved with 4 percent persulfate. Thus, for the following larger-scale runs with various weights of blue stock, the persulfate was applied at the 4-percent level.

FINISHING OF GRAFTED LEATHERS

Having established the optimum level of pretreatment with persulfate and the optimum molar ratio of sodium bisulfite to persulfate, the next step was to graft-polymerize side-leather blue stock in large enough runs to put through dyeing, fatliquoring, and finishing. A number of runs were made with both lightweight (2 oz) and heavier (up to 5.5 to 6 oz) sides. They were treated in accordance with the following recipe:

	Percent
Side-leather blue stock	100
$K_2S_2O_8$	4
Float	800
Drum 6 hr, drop float, horse up overnight	
Refloat	800
Emulphogene 840 BC	0.5
Purge with CO_2 to < 1 percent O_2	
$NaHSO_3$	0.28
Add in small reserved part of float while drumming.	
Continue to drum 30 min, then add while drumming:	
Methyl methacrylate plus methacrylic acid (9:1)	15 to 25
Dermalite Brown 2GL	5
Drum 5 hr	

In the early, small-scale experiments, only methyl methacrylate was used to permit meaningful comparisons for total and bound polymer and for evaluating graft efficiency among the various runs. In these larger-scale runs this monomer was combined with methacrylic acid, a comonomer capable of reducing polymer extractability (5). The lower level of monomer was used for the lighter sides, the higher for the heavier sides.

In an earlier study (6) with sheepskin, amphoteric compounds such as Deriphat 151C® * were found to be useful fatliquors. These same compounds are not as effective in lubricating side leather. For the grafted side leathers a blend of Nutreen-X and raw neatsfoot oil (8 and 3.7 percent respectively, based on the stock's average dry substance) was used. With the 3- to 6-oz side, an additional 2.5 percent of CL-2 oil was added. These fatliquors were chosen from limited trials and may not be the best possible.

The sides were set out and staked before being finished. A conventional base coat was not needed because of the presence of the grafted polymer. The coating formulas used are given in Table IV. No problems were found in plating. As with the fatliquor, the choice of finish coats was somewhat limited. Probably improved coats will be found. In any case, the leather had a very good break and a natural aniline look.

In summary, persulfate ion can be absorbed into blue stock at the 4- percent level and can be used for at least three months in a redox-initiated graft polymerization. Since this initiation takes place within the leather, improved graft efficiency is obtained when low levels of bisulfite are used. In addition, conditions giving full penetration by the persulfate ion improve polymer distribution. The presence of this grafted polymer makes the leather more compatible to finishing and obviates the need for the conventional base coat.

* Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

TABLE IV

COATING FORMULAS FOR GRAFTED LEATHER

First Coat[a]	Second Coat[b]
30 parts Hydrholac WC-300	4 parts product WU 2500
10 parts water	4 parts product WU 2501
1½ parts Orange V dye	1 part 55 wax
¾ part Blue V dye	16 parts water

[a] Use 2 spray coats and dry after each.
[b] Use 1 wet coat, dry and Turner press for 3 sec at 200°F.

Acknowledgments

The authors thank Edward Diefendorf for his part in fatliquoring and finishing the side leathers and for his helpful suggestions in general.

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Received April 24, 1981

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